PATENT SPECIFICATION

(11) 1 395 609

1 395 609

(21) Application No. 31533/72 (22) Filed 5 July 1972
(31) Convention Application No. 49444/71 (32) Filed 5 July 1971
(31) Convention Application No. 57014/71 (32) Filed 29 July 1971
(31) Convention Application No. 64267/71 (32) Filed 23 Aug. 1971 in
(33) Japan (JA)
(44) Complete Specification published 29 May 1975
(51) INT CL² C08L 27/14; C08K 5/00, C08L 27/20; C09D 3/78
(52) Index at acceptance
C3P 10C13C 10C14B 10C16C 10C17 10C18 10C20A 10C20C 10C20D1 10C20D3 10C4A 10C7 10C8B 10C8C 10D1X 10D2X 10D5 10D8 10K10 10K4 10K8 10T2A 11C14B 11C17 11C20C 11C20D1 11C7 11C8B 11C8C 11D2A2A 11D8 11K10 11T2A 4C14B 4C20A 4D3B1 4D8 4K10 8C12X 8C14B 8C17 8C20C 8C20D1 8C20D3 8C7 8C8B 8C8C 8D1A 8D2B1 8D8 8K10 8T2A E2

(19)

(54) NEW COATING COMPOSITIONS

(71) We, TEIJIN LIMITED, a Japanese Body Corporate of No. 1 Umeda-Kita-Ku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a liquid coating composition containing vinyl fluoride-hexafluoropropylene resin which has superior storage stability even in high concentrations and can form a coating layer having outstandingly superior mechanical strength properties such as tensile strength, initial Young's modulus or hardness and superior transparency and gloss.

Generally, fluorine resins have excellent resistance to chemicals and weather and electrical properties, and have special utility. Because of superior weatherbility compared with other resins, the fluorine resins are expected to be useful in the field of coating, and the development of this utility has recently attracted attention. However, the fluorine resins have the disadvantage of having poor processability and solubility.

Generally, polyvinyl fluoride and polyvinylidene fluoride have similar mechanical properties, but have very different solubilities. At room temperature, polyvinyl fluoride is insoluble in almost all solvents, but polyvinylidene fluoride has relatively superior solubility. It is soluble at room temperature in a solvent such as N,N-dimethyl formamide or N,N-dimethyl acetamide in a concentration of up to about 15% by weight. It is well known that at elevated temperatures, polyvinylidene fluoride becomes soluble in a wider variety of solvents.

Liquid coating compositions containing vinylidene fluoride-hexafluoropropylene copolymer have previously been known (see British Patent 871,582, British Patent 1,001,765, U.S. Patent 3,194,796, and French Patent 1,350,581).

The first-mentioned British Patent discloses that a coating composition comprising an elastomer of a copolymer of from 30 to 70% by weight of vinylidene fluoride and from 70 to 30% by weight of hexafluoropropylene in a methyl ethyl ketone-toluol mixed solvent or methyl isobutyl ketone-toluol mixed solvent is useful for coating aromatic polyamide fabrics. The latter-mentioned British Patent to which the U.S. Patent and French Patent mentioned correspond discloses a liquid coating composition comprising a copolymer composed of 45—80% by weight of vinylidene fluoride, 0.05 to 2% by weight of a monomer selected from acrylonitrile, glycidyl methacrylate and ethylene dimethacrylate, and the remainder being hexafluoropropylene and a solvent such as acetone, ethyl acetate, acetic acid, methyl ethyl ketone, lower-molecular-weight esters, aldehyde, organic acid, etc.

However, the liquid coating composition containing a vinylidene fluoride-hexafluoropropylene copolymer has very poor storage stability, and especially when the concentration of the copolymer is high, cannot at all withstand storage for prolonged periods of time. Coated layers prepared from this composition have no satisfactory mechanical strength, such as tensile strength, initial Young's modulus or hardness, and their transparency and gloss are still required to be improved.

According to the present invention there

is provided a liquid coating composition comprising a vinyl fluoride/hexafluoropropylene copolymer having an inherent viscosity (measured as hereinafter defined) of 0.1 to 2 and composed of (i) 5 to 50 mol % of units derived from hexafluoropropylene, (ii) 0 to 10 mol % of units derived from a vinyl ester of an aliphatic carboxylic acid, in which the acid portion has 1 to 6 carbon atoms, or 0 to 1 mol % of units derived from a monomer which is selected from unsaturated aliphatic carboxylic acids having 3 to 6 carbon atoms, glycidyl acrylate and glycidyl methacrylate and (iii) the remainder being units derived from vinyl fluoride, and a solvent for the copolymer which is one or more of (1) an aliphatic ketone having not more than 9 carbon atoms, (2) an alkyl ester of an aliphatic monocarboxylic acid or a halide thereof, the said ester having not more than 10 carbon atoms, (3) an alkyl ester of an aliphatic dicarboxylic acid, the acid residue having 2 to 7 carbon atoms and each alkyl group having not more than 3 carbon atoms, (4) an aliphatic monocarboxylic acid having 2 to 4 carbon atoms or an anhydride thereof, (5) a cyclic ether, (6) an aliphatic nitrile having 2 to 6 carbon atoms, and (7) a compound selected from dialkyl esters of carbonic acid, wherein the alkyl groups together contain 2 to 4 carbon atoms, ethylene carbonate, cyclohexanone, N,N-dimethyl formamide, N,N-dimethyl acetamide, dimethyl sulfoxide, N-methyl pyrrolidone and γ-butyrolactone, the amount of the said copolymer being 1 to 50% by weight, as solids content, based on the weight of the composition. The amount of component (i) is preferably 10 to 50 mol %. Such a composition shows very superior storage stability; and a coated layer prepared from such a composition has improved mechanical strength such as tensile strength, initial Young's modulus and hardness and also transparency and gloss over that of a vinylidene fluoride-hexafluoropropylene resin liquid coating composition. This is quite unexpected in view of the fact that polyvinyl fluoride and polyvinylidene fluoride have similar mechanical strength, but polyvinyl fluoride is far less soluble than polyvinylidene fluoride.

The copolymer used in this invention has an inherent viscosity of 0.1 to 2, preferably 0.1 to 1.

Examples of the vinyl esters of aliphatic carboxylic acids are vinyl acetate, vinyl propionate, vinyl butyrate, and vinyl caproate.

Examples of the unsaturated aliphatic carboxylic acids are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, fumaric acid and maleic acid.

The vinyl fluoride-hexafluoropropylene copolymer can be produced by any means known in the art. For example, it can be prepared by aqueous suspension polymerization of 5 to 50 mol % of hexafluorpropylene, 0 to 10 mol % of the said vinyl ester or 0 to 1 mol % of the said other monomer (ii), and 50 to 95 mol % of vinyl fluoride in the presence of a known organic peroxide initiator, such as diisopropyl peroxydicarbonate, tertiary butyl peroxypivalate, lauryl peroxide, ditertiary butyl peroxide, isobutyl peroxide, di-(2-ethylhexyl)-peroxydicarbonate or di-(2-ethoxyethyl)-peroxydicarbonate. The reaction temperature used most frequently is about 10° to 100°C. Preferably, the aqueous suspension polymerization is carried out in the copresence of a fluorine-containing surface active agent and a dispersing agent in order to obtain a homogeneous copolymer.

If the copolymerization of vinyl fluoride and hexafluoropropylne is carried out using only a dispersing agent such as methyl cellulose or polyvinyl alcohol without adding a fluorine-containing surface active agent, the resulting copolymer is non-uniform, and the formation of a mixture of a polymer containing a major proportion of vinyl fluoride units and a copolymer containing a minor proportion of vinyl fluoride units is observed. In fact, this copolymer mixture is separable into a portion which is soluble in methyl ethyl ketone and a portion which is not.

On the other hand, if the copolymerization is carried out using only the fluorine-containing surface active agent without using the dispersing agent, the resulting copolymer is in the form of relatively uniform powders, but a scale-like thin layer of the polymer tends to adhere to the wall of the reaction vessel and the polyer is difficult to handle. Also, the polymer contains a portion insoluble in methyl ethyl ketone although in a very slight amount.

The conjoint use of the fluorine-containing surface active agent and the dispersing agent together with the organic peroxide initiator can lead to a homogeneous copolymer of vinyl fluoride and hexafluoropropylene. Scales do not adhere to the reaction vessel, and it is easy to separate and recover the copolymer.

For the purpose of adjusting the degree of polymerization of the copolymer, a compound such as trichlorofluoromethane, 1,2-difluoro-1,1,2,2-tetrachloroethane, or 1,1,2-trifluoro-1,2,2-trichloroethane may be present in the reaction system. If carbon tetrachloride or mercaptan, which are generally known as chain transfer agents in the polymerization of vinyl compounds, are used, the polymerization is inhibited, or the resulting copolymer is liable to be coloured.

The preferred amount of such a compound is 0.5 to 50 parts by weight per 100 parts by weight of the total amount of the monomers, the amount of 1 to 40 parts by weight being especially preferred.

Examples of the fluorine-containing surface active agent are water-soluble salts of polyfluorinated aliphatic carboxylic acids and water-soluble salts of polyfluorochlorinated aliphatic carboxylic acids, such as the sodium salt of perfluorooctanoic acid or the sodium salt of perfluoroalkylsulfonic acid, and phosphoric acid esters or sulfuric acid esters of polyfluorinated or polyfluorochlorinated aliphatic alcohols.

Examples of the dispersing agent include methyl cellulose, gelating, tragacanth, starch, carboxymethyl cellulose, polyvinyl alchol, partial saponified polyvinyl alcohol, and polyacrylic acid. Other known dispersing agents used in the aqueous suspension polymerization of vinyl monomers can be used.

The amount of the fluorine-containing surface active agent is from about 0.05% by weight to about 2% by weight based on the total amount of the monomers.

The amount of the dispersing agent is preferably from about 0.1 to about 3.0% by weight based on the total amount of the monomers.

The weight ratio of the dispersing agent to the fluorine-containing surface active agent is preferably 1—2.

Vinyl fluoride-hexafluoropropylene copolymers containing less than 5 mol % of units derived from hexafluoropropylene prove unsuitable because of very poor solubility in solvents. Copolymers of vinyl fluoride and hexafluoropropylene containing more than 50% of units derived from hexafluoropropylene have increased solubility, but a coated layer obtained from a solution of this copolymer has a very soft and weak surface which has a low softening point and is useless.

The vinyl ester and the other monomer (ii) which may be contained in the vinyl fluoride-hexafluoropropylene copolymer of this invention in amounts of not more than 10 mol % and not more than 1 mol % respectively, can be utilized to improve the hardness, adhesion to the base material, etc., of the resulting coated layer.

The vinyl fluoride-hexafluoropropylene copolymer used in this invention has an inherent viscosity of 0.1 to 2, preferably 0.1 to 1, more preferably 0.2 to 0.7. The inherent viscosity (η inh) is measured at 30°C. with respect to a solution of 0.5 g of the copolymer in 100 ml of dimethyl formamide, and is expressed by the following equation

$$\eta\ \mathrm{inh} = \frac{1}{C} \ln \frac{t}{t_0}$$

wherein C (0.5 g/100 ml.) is the concentration of the polymer, t (seconds) is the flow time of N,N-dimethyl formamide solution of the polymer, and t_0 (seconds) is the flow time of N.N-dimethyl formamide.

If the inherent viscosity of the copolymer used is lower than 0.1, the film on the surface of a coated layer is weak, and the coating effect is not fully achieved. If the inherent viscosity is higher than 2, a solution of the copolymer has high viscosity, and the handling of the liquid coating composition or the coating operation becomes extremely difficult. Especially when such a solution is applied by spray coating, the surface of the coat exhibits a pattern of randomly arranged yarns, and it is extremely difficult to form a uniform coating film. Generally, copolymers having an inherent viscosity within this range are of relatively low molecular weight, and have somewhat unsatisfactory mechanical properties for general uses. It has however been found that for application as coating agents, copolymers of such inherent viscosities are superior in every respect.

The solvent for use in the preparation of the liquid coating composition of this invention is selected from (1) aliphatic ketones having not over 9 carbon atoms, (2) alkyl esters of aliphatic monocarboxylic acids and halides thereof, the said esters having not more than 10 carbon atoms, (3) C_{1-3} alkyl esters of C_{2-7} aliphatic dicarboxylic acids, (4) aliphatic monocarboxylic acids having 2 to 4 carbon atoms and anhydrides thereof, (5) cyclic ethers, (6) aliphatic nitriles having 2 to 6 carbon atoms, and (7) dialkyl esters of carbonic acid in which the alkyl groups together contain 2—4 carbon atoms, ethylene carbonate, cyclohexanone, N,N-dimethyl formamide, N,N-dimethyl acetamide, dimethyl sulfoxide, N-methyl pyrrolidone and γ-butyrolactone. These solvents may be used alone or in combination, and a combination of these frequently gives good results.

It is preferred that the copolymer be used as a solution, but it can also be used as a suspension or emulsion. In the latter case, a small amount of one or more of non-solvents such as xylene, toluene and n-hexane can be used.

Examples of the aliphatic ketones having not over 9 carbon atoms are acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl isopropyl ketone and diisobutyl ketone. Aliphatic ketones having 10 or more carbon atoms or aromatic ketones such as methylphenyl ketone are undesirable because of poor solubility or

too high boiling points which cause difficulty in drying the coated film.

Examples of the alkyl esters of aliphatic monocarboxylic acids and halides thereof are methyl formate, ethyl acetate, butyl acetate, butyl propionate, isoamyl acetate, isoamyl butyrate, ethyl monochloroacetate and ethyl trichloroacetate. Alkyl esters of aliphatic monocarboxylic acids having 11 or more carbon atoms, for example aliphatic monocarboxylic acid esters or halides thereof, such as methyl laurate or n-butyl stearate, and aromatic carboxylic acid esters or halides thereof, such as methyl benzoate or methyl salicylate have inferior ability to dissolve the copolymer, and these aliphatic monocarboxylic acid esters having more carbon atoms are inadequate because of high boiling point and low volatility.

Examples of the alkyl esters of aliphatic dicarboxylic acids having 2 to 7 carbon atoms are diethyl oxalate, diethyl malonate, and diisopropyl malonate. Esters of aliphatic dicarboxylic acids having 8 or more carbon atoms also dissolve the copolymer well, but are inadequate for use in the present invention because of high boiling points and difficulty of volatilization

Examples of the aliphatic monocarboxylic acids having 2 to 4 carbon atoms and anhydrides thereof are acetic acid, propionic acid, butyric acid and acetic anhydride. Formic acid having one carbon atom and aliphatic monocarboxylic acids having 5 or more carbon atoms and anhydrides thereof are unsuitable because of extremely poor ability to dissolve the copolymer.

Examples of the cyclic ether are dioxane, and tetrahydrofuran. Aliphatic ethers such as ethyl ether are totally unable to dissolve the copolymer, and therefore useless in the present invention.

Examples of the aliphatic nitriles having 2 to 6 carbon atoms are acetonitrile, butyronitrile, valeronitrile, and capronitrile. Aliphatic nitriles having 7 or more carbon atoms and aromatic nitriles have small ability to dissolve the copolymer and cannot form solutions of high concentrations, and also have high boiling points and difficulty of volatilization.

The preferred solvent is at least one relatively low boiling solvent selected from aliphatic ketones having 7 or less carbon atoms, aliphatic monocarboxylic acid esters, aliphatic nitriles and cyclic ethers, or a mixture of it with another solvent specified above in which the amount of the said low boiling solvent is at least 40% by weight. Especially, this mixed solvent makes it possible to control the rate of volatilization moderately, and therefore, the loss of transparency of the coated layer can be easily prevented.

As previously stated, the liquid coating composition of this invention is a liquid comprising 1 to 50% by weight, preferably 1 to 40% by weight, of a copolymer of vinyl fluoride and hexafluoropropylene having the above-specified inherent viscosity, and the said solvent. A composition containing the said copolymer in a concentration of more than 50% by weight has high viscosity, and is difficult to handle. Those compositions containing the copolymer in a concentration lower than 1% by weight are undesirable in the procedure of forming a coating layer since the amount of the solvent that has to be volatilized is too large.

The liquid coating composition of this invention may contain up to 5% by weight, based on the weight of the composition, of other resin which is soluble in the solvents used in the invention, in order to control the viscosity of the composition, the adhesiveness of the coated layer, and its hardness and strength properties. Examples of the additional resin are homo- or copolymers of acrylic acid, methacrylic acid, or esters of such acids, homo- or copolymers of aromatic vinyl compounds such as styrene or α-methyl styrene, homo- or copolymers of halogen-containing vinyl compounds such as vinyl fluoride, vinylidene fluoride, trifluorochloroethylene, tetrafluoroethylene, vinyl chloride or vinylidene chloride, and chlorinated rubber.

The liquid coating composition of this invention may also contain additives employed customarily, such as colouring agents (dyes, pigments), viscosity control agents, wetting agents, rust-proof agents, or defoaming agents. The liquid coating composition of this invention may also contain a cross-linking agent or a cross-linking promotor. Specific examples of such additives are inorganic pigments such as red iron oxide, micaceous iron oxide, chrome yellow, Prussian Blue, Ultramarine Blue, zinc chromate, molybdenum red, titanium white, barytes, precipitated barium sulfate, barium carbonate, carbon black, whiting, precipitated calcium carbonate, gypsum, asbestine, china clay, silica, white carbon, kieselguhr, talc, magnesium carbonate, alumina white, glass white, satin white, zinc oxide, basic lead carbonate, basic lead sulfate, lead sulfate, lithopone, zinc sulfide, antimony oxide, cadmium yellow, calcium plumbate, red lead, cadmium red, chrome green, aluminium powder, bronze powder, copper powder, tin powder, lead powder, zinc dust, zinc tetraoxychromate, zinc phosphate or strontium chromate; organic

pigments such as Permanent Red F4R, Lake Red C, Lithol Red R, Brilliant Carmine BS, Pigment Scarlet 3B, Pyrazolone Red, Pyrazolone Orange G, Benzidine Orange 2G, Hanza Yellow 3R, Alkali Blue Lake, Phthalocyanine Blue, Phthalocyanine Green or Bordeaux 10B; viscosity control agents such as amine treated clays, for example Bentone (Trade Mark) 34, Bentone 38 (National Lead Co.,), vegetable oil derivatives, for example Dehysol R, Ceroxin Special (Henkel International GmbH), Thixcin (Trade Mark) R, Thixatrol ST, Post-4 (The Baker Caster Oil Co.,), metal soaps such as aluminium stearate, xylene, toluene, or n-hexane; wetting agents such as lecithin, surface active agents for example ANTITERRA—A, ANTITERRA—P(BYK—Mallinkvodt); plasticize: plasticizers, for example, phthalic acid esters such as dimethyl phthalate, dibutyl phthalate, or dioctyl phthalate, phosphoric acid esters such as trichloroethyl phosphate or triphenyl phosphate, glycolic acid esters such as methyl phthalyl glycolate or ethyl phthalyl ethyl glycolate, or glycol derivates such as ethyl glycol or butyl glycol; light stabilizers, for example, salicylic acid type ultraviolet absorbers such as Inhibibor OPS (p-octyl phenyl salicylate, Eastman Chemical Products, Inc), Light Absorber TBS (4-tert.-butyl phenyl salicylate Dow Chemical Company), benzophenone type ultraviolet absorbers such as Cyasorb UV—9, UV—24, UV—207 and UV—284 (2-hydroxy-4-methoxy benzophenone, American Cyanamid Company), benzotriazole type ultraviolet absorbers such as Tinuvin (Trade Mark) P [2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, Geigy], other ultraviolet absorbers such as Cyasorb UV—1084 [2,2'-thiobis(4-tert-octyl phenolate)]n-butylamine Ni, Inhibitor RMB (resorcinol monobenzoate, Eastman Chemical Products Inc.), antioxidants, for example, amine-type antioxidants such as phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, ketone-amine condensate type antioxidants such as 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline, a polymer of 2,2,4-trimethyl-1,2-dihydroquinoline, aldehyde-amine condensate type antioxidants such as aldol-alpha-naphthylamine, mixed amine type antioxidants such as Akroflex C, Cb, F (Du Pont) or Thermaflex A (Du Pont), phenolic antioxidants such as 2,4-dimethyl-6-tert-butyl phenol or 2,6-ditert.-butyl-p-cresol, and other antioxidants such as polycarbodiimide, propyl gallate or tri(nonylated phenyl) phosphite; and defoamers such as Toray Silicon DC 7 (Toray Industries, Inc.), Toray Silicon OH 5540 (Toray Industries, Inc.) or BYK—SL (BYK—Mallinckrodt).

Examples of the cross-linking agent are aliphatic polyamines such as methylene diamine, ethylene diamine, tetramethylene diamine, hexamethylene diamine, triaminopropane, tris(2-aminoethyl)amine, diethylene triamine or triethylene tetramine, aromatic polyamines such as o-, m- and p-phenylene diamines, triaminobenzene, pentaminobenzene or tolylene diamine, and carbamates of said polyamines such as hexamethylene diamine carbamate. Examples of the cross-linking accelerator are basic divalent metal oxides such as magnesium oxide, calcium oxide, lead oxide or barium oxide, basic metal hydroxides such as magnesium hydroxide, calcium hydroxide or barium hydroxide, or macrocyclic compounds such as 2,5,8,15,18,21 - hexaoxatricyclo[20,4,0,0] - hexacone or 2,5,8,11 - tetraoxabicyclo - [21,0,4,0]hexadecane.

The amount of the cross-linking agent is about 0.1 to 10% by weight based on the weight of the vinyl fluoride/hexafluoropropylene copolymer. The amount of the cross-linking promoter is about 5 to about 50% by weight based on the weight of said copolymer, if the cross-linking agent is used in the above-mentioned amount. Cross-linking occurs at room temperature, and therefore, it is not necessary to conduct it as elevated temperatures. But is is possible to conduct it at an elevated temperature up to 300°C. after a coating is formed and the solvent evaporated.

The coating of the liquid composition on a base material can be performed by any desired method known in the art, such as brush coating, spray coating, roller coating, casting, or immersion.

The liquid composition of this invention can be applied directly to the base material, but may also be applied thereto through a primer in order to improve the adhesion of the coating to the base material or the flexibility of the coated film.

For example, the primer may comprise a coating of a copolymer of 95—40% by weight of methyl methacrylate and 5 to 60% by weight of at least one unsaturated monomer selected from methacrylic acid esters other than methyl methacrylate, acrylic acid esters and unsaturated compounds containing a free carboxyl group.

Examples of the acrylic acid esters are methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, and dodecyl acrylate. Examples of the methacrylic acid esters are ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, and dodecyl methacrylate.

The unsaturated compound containing a free carboxyl group may be any compound which can be copolymerized with methyl methacrylate, examples of which are acrylic acid, methacrylic acid, itaconic acid,

fumaric acid or maleic acid.

The primer may be of a solution-type acrylic lacquer or an aqueous dispersion type acrylic emulsion.

Furthermore, the primer may consist of two undercoat layers, a first layer consisting of at least one primer selected from epoxy resin type primers, nitrocellulose type primers and acrylic type primers, and a second layer consisting of a mixture of a copolymer of hexafluoropropylene and vinylidene fluoride soluble in methyl ethyl ketone and a copolymer of methyl methacrylate and an acrylic acid ester and/or a methacrylic acid ester other than the methyl methacrylate containing 0 to 30% by weight of an unsaturated monomer containing a free carboxyl group, the weight ratio of the first-mentioned copolymer to the second-mentioned copolymer being 1:99 to 40:60.

As the unsaturated monomer containing a free carboxyl group, the acrylic acid ester and the methacrylic acid ester, those exemplified above can be utilized.

In an alternative embodiment, the primer may consist of a first layer comprising either one of zinc chromate or chromic anhydride, polyvinyl butyral, alcohol, phosphoric acid and water, and a second layer comprising a copolymer of methyl methacrylate and an acrylic acid ester and/or a methacrylic acid ester other than methyl methacrylate. The same acrylic acid esters and methacrylic acid esters as exemplified above may be used for this purpose.

The liquid coating composition of this invention can form a coated layer having extremely high mechanical strength such as tensile strength, initial Young's modulus and hardness and remarkably improved transparency and gloss. This liquid coating composition exhibits excellent storage stability even in high concentrations of the resin. Furthermore, the coated layer has good weatherability, resistance to chemicals, electric characteristics and thermal stability inherently possessed by fluorine resins.

The liquid coating composition of this invention is useful for forming a coating on the surface of various base materials such as metals, wood, plastics, glass or ceramics, and can also be utilized for surface coating of fibers, yarns, knitted and woven fabrics, non-woven fabrics, and other filamentary structures. The viscosity of the liquid coating structure can be varied according to the field for which the composition is intended, and also according to the types and amounts of additives. Usually, it may be 10 to 5000 centipoises.

The present invention will be illustrated by the following Examples and Comparative Examples.

The various properties of the coated layer and the liquid composition were determined as follows:

(1) Tensile Strength and Initial Young's Modulus

Measured in accordance with JIS K—6723 using an Instron universal tensile tester.

(2) Hardness

A composition was prepared by mixing 30 parts by weight of a vinyl fluoride-hexafluoropropylene copolymer, 70 parts by weight of a solvent and 10 parts by weight of titanium oxide (Tipaque [Trade Mark] R—820 Ishihara Sangyo Kaisha Ltd.) in a ball mill for 20 hours. The composition was coated on a polished steel plate, and air dried for 48 hours. Thereafter, the hardness of the coated layer was measured in accordance with JIS G—3312.

(3) Transparency

A film having a thickness of 25 microns was prepared from the composition of this invention by the casting method, and the percent transmission at 600 mμ of this film was measured.

(4) Gloss

The same composition as shown in (2) above was coated on a polished steel sheet and air dried for 48 hours, and then the gloss was measured in accordance with JIS K—5400.

(5) Storage stability

10—30 parts by weight of the vinyl fluoride/hexafluoropropylene copolymer was dissolved in 70—90 parts by weight of a solution. The solution was left to stand at room temperature (18°C), and the time required until the occurrence of gellation of the solution was measured.

Example 1.

Preparation of Copolymer:—

A 100 ml. autoclave was completely purged with nitrogen, and then charged with 65 g of deoxygenated water, 0.15 g of methyl cellulose, 0.1 g of sodium perfluorooctanesulfonate, and 0.237 g of diisopropyl peroxidicarbonate. These compounds were frozen in a dry ice methanol coolant in a stream of nitrogen. A lid was mounted on the autoclave, and the autoclave was carefully purged with nitrogen under reduced pressure. The inside of the autoclave was maintained at reduced pressure and in the frozen state. Separately prepared vinyl fluoride (12.9 g; 0.281 mol) and hexafluoropropylene (10.8 g; 0.072 mol) were charged successively into the autoclave by means of distillation, as follows: a measuring tube made of pressure-resistant glass is cooled to −78°C. and the prescribed amount of monomer is charged thereto. The measuring tube is connected, via a pressure-resistant introduction tube, to a

stainless steel autoclave containing water, dispersant and catalyst in predetermined amounts. The autoclave is cooled to −78°C. and simultaneously the measuring tube is warmed up to 0°C., whereupon the monomer distils.

The temperature in the autoclave was returned to room temperature, and the reaction mixture was rapidly subjected to a rotary constant-temperature shaking apparatus at 50°C., and the polymerization reaction was carried out for 8 hours.

The polymerization yield was 84.0%, and the inherent viscosity of the resultant polymer was 0.72.

Example 2.

Preparation of Copolymer:—

The copolymerization reaction was carried out at 50°C. for 8 hours in the same way as set forth in Example 1 except that a 300 ml. autoclave was used, and 33.5 g (0.729 mol) of vinyl fluoride, 45.4 g (0.302 mol) of hexafluoropropylene, 0.789 g of diisopropyl peroxidicarbonate, 0.4 g of methyl cellulose, 0.3 g of sodium perfluorooctanesulfonate, and 165 g of deoxygenated water were used.

There was obtained 63.2 g (polymerization yield 80.1%) of a white granular copolymer having an inherent viscosity of 0.70.

Example 3.

Preparation of Copolymer:—

A 100 ml. autoclave was completely purged with nitrogen and charged with 65 g of deoxygenated water, 0.2 g of methyl cellulose, 0.1 g of sodium perfluorooctanesulfonate, 0.263 g of diisopropyl peroxidicarbonate, and 3 g of trichlorofluoromethane. These compounds were frozen in a dry ice methanol coolant in a stream of nitrogen. The autoclave was purged carefully with nitrogen at reduced pressure. The inside of the autoclave was maintained at reduced pressure and in the frozen state. Separately prepared vinyl fluoride (11.2 g; 0.243 mol) and hexafluoropropylene (15.1 g; 0.10 mol) were charged successively into the autoclave by means of distillation as described in Example 1. After charging, the temperature was returned to room temperature, and the reaction mixture was subjected quickly to a rotary constant temperature shaker at 50°C. The polymerization reaction was conducted, and after a lapse of 8 hours, the unreacted monomers were recovered. The polymerization yield was 76.0%, and the resulting copolymer was composed of white granules having an inherent viscosity of 0.29.

Example 4.

Preparation of Copolymer:—

The polymerization reaction was carried out for 8 hours at 50°C. in the same way as set forth in Example 1 except that 70 g of deoxygenated water, 0.24 g of methyl cellulose, 0.15 g of sodium perfluorooctanesulfonate, 0.265 g of diisopropyl peroxidicarbonate, 1.5 g of trichlorofluoromethane, 12.9 g (0.28 mol) of vinyl fluoride, and 13.6 g (0.091 mol) of hexafluoropropylene were used. The polymerization yield was 77.0%, and there was obtained a white granular copolymer having an inherent viscosity of 0.42.

Example 5.

Preparation of Copolymer:—

The polymerization reaction was carried out for 8 hours at 50°C. in the same way as set forth in Example 1 except that 12.9 g (0.281 mol) of vinyl fluoride, 10.8 g (0.072 mol) of hexafluoropropylene and 0.16 g (0.0011 mol) of glycidyl methacrylate were used. The polymerization yield was 85%, and there was obtained a white granular copolymer having an inherent viscosity of 0.53.

Examples 6 to 15 and
Comparative Examples 1 to 21.

A stirrer-equipped flask was charged with 30 parts by weight of a copolymer having an inherent viscosity of 0.71 and derived from 70.7 mol % of vinyl fluoride and 29.3 mol % of hexafluoropropylene and 70 parts by weight of methyl ethyl ketone, and these compounds were stirred at 20°C. There was easily obtained a colorless clear liquid coating composition.

Similar liquid coating compositions were prepared using various different copolymers and solvents. The results of the tests (i) to (v) mentioned above are shown in Table 1.

In the following tables, the following abbreviations are used.

VF:	vinyl fluoride
HFP:	hexafluoropropylene
VDF:	vinylidene fluoride
GMA:	glycidyl methacrylate
AA:	acrylic acid
VAc:	vinyl acetate

TABLE 1.

No.	Liquid Coating Composition								
	Resin Component								
	1st component		2nd component		3rd component		Inherent viscosity (η inh)	Resin concentration (% by wt.)	Solvent
	Kind	mol %	Kind	mol %	Kind	mol %			
Ex. 6	VF	70.7	HFP	29.3	—	—	0.71	30	Methyl ethyl ketone
Comp. Ex. 1	VF	100	—	—	—	—	—	—	Methyl ethyl ketone
Comp. Ex. 2	VDF	70.7	HFP	29.3	—	—	0.67	30	Methyl ethyl ketone
Ex. 7	VF	90.5	HFP	9.5	—	—	0.81	10	Acetone
Comp. Ex. 3	VDF	90.5	HFP	9.5	—	—	0.74	10	Acetone
Comp. Ex. 4	VF	95.8	HFP	4.2	—	—	0.80	10	Acetone
Comp. Ex. 5	VF	44.7	HFP	55.3	—	—	0.61	30	Acetone
Ex. 8	VF	74.7	HFP	25.0	GMA	0.3	0.52	30	Methyl isobutyl ketone
Comp. Ex. 6	VDF	74.7	HFP	25.0	GMA	0.3	0.50	30	Methyl isobutyl ketone
Ex. 9	VF	68.3	HFP	31.7	—	—	0.73	30	Cyclohexanone
Comp. Ex. 7	VDF	68.3	HFP	31.7	—	—	0.63	30	Cyclohexanone
Comp. Ex. 8	VF	68.3	HFP	31.7	—	—	0.73	10	Methyl phenyl ketone
Ex. 10	VF	70.7	HFP	29.3	—	—	0.71	30	Ethyl formate
Comp. Ex. 9	VDF	70.7	HFP	29.3	—	—	0.67	30	Ethyl formate
Ex. 11	VF	90.5	HFP	9.5	—	—	0.81	10	Ethyl acetate

TABLE 1 (continued).

No.	Liquid Coating Composition								
	Resin Component								
	1st component		2nd component		3rd component		Inherent viscosity (η inh)	Resin concentration (% by wt.)	Solvent
	Kind	mol %	Kind	mol %	Kind	mol %			
Comp. Ex. 10	VDF	90.5	HFP	9.5	—	—	0.74	10	Ethyl acetate
Comp. Ex. 11	VF	95.8	HFP	4.2	—	—	0.80	10	Ethyl acetate
Ex. 12	VF	55	HFP	45	—	—	0.63	30	Butyl acetate
Comp. Ex. 12	VDF	55	HFP	45	—	—	0.53	30	Butyl acetate
Ex. 13	VF	74.7	HFP	25.0	GMA	0.3	0.70	30	Isoamyl acetate
Comp. Ex. 13	VDF	74.7	HFP	25.0	GMA	0.3	0.67	30	Isoamyl acetate
Comp. Ex. 14	VF	73.4	HFP	25.0	GMA	1.6	0.66	10	Isoamyl acetate
Ex. 14	VF	80	HFP	20	—	—	0.63	20	Butyl propionate
Comp. Ex. 15	VDF	80	HFP	20	—	—	0.66	20	Butyl propionate
Comp. Ex. 16	VF	97	HFP	3	—	—	0.78	10	Butyl propionate
Comp. Ex. 17	VF	42	HFP	58	—	—	0.60	30	Butyl propionate
Ex. 15	VF	58	HFP	42	—	—	0.55	30	Ethyl chloroacetate
Comp. Ex. 18	VDF	58	HFP	42	—	—	0.51	30	Ethyl chloroacetate
Comp. Ex. 19	VF	80	HFP	20	—	—	0.63	20	Methyl salicylate
Comp. Ex. 20	VF	80	HFP	20	—	—	0.63	20	Methyl laurate
Comp. Ex. 21	VF	80	HFP	20	—	—	0.63	20	Benzyl acetate

TABLE 1 (continued).

No.	Properties				
	Storage stability (hr)	Tensile strength (Kg/cm²)	Elongation (%)	Initial Young's modulus (kg/cm²)	Transparency (%)
Ex. 6	over 720	220	273	2,340	89
Comp. Ex. 1		(Insoluble)			
Comp. Ex. 2	10	108	439	14	58
Ex. 7	360	340	269	4,300	90
Comp. Ex. 3	6	180	317	70	61
Comp. Ex. 4		(Partially insoluble)			
Comp. Ex. 5	over 720	101	430	60	88
Ex. 8	over 720	228	316	3,120	90
Comp. Ex. 6	6	106	428	61	57
Ex. 9	360	230	306	2,430	90
Comp. Ex. 7	5	95	630	13	58
Comp. Ex. 8		(Partially insoluble)			
Ex. 10	480	220	273	2,340	88
Comp. Ex. 9	3	108	439	14	50
Ex. 11	240	340	269	4,300	87
Comp. Ex. 10	6	180	317	70	52
Comp. Ex. 11		(Partially insoluble)			
Ex. 12	over 720	180	531	631	91
Comp. Ex. 12	10	84	738	12	62
Ex. 13	240	228	316	3,120	86
Comp. Ex. 13	3	106	428	61	59
Comp. Ex. 14		(Partially insoluble)			
Ex. 14	240	294	215	4,500	89
Comp. Ex. 15	6	112	531	30	60
Comp. Ex. 16		(Insoluble)			
Comp. Ex. 17	over 720	80	432	52	87
Ex. 15	360	182	269	113	83
Comp. Ex. 18	6	78	438	11	59
Comp. Ex. 19		(Partially insoluble)			
Comp. Ex. 20		(Insoluble)			
Comp. Ex. 21		(Partially insoluble)			

Examples 16 to 41 and Comparative Examples 22 to 63.

Liquid coating compositions were prepared using copolymers of various ratios of copolymer units and various solvents both indicated in Table 2. The results are also shown in Table 2.

TABLE 2.

No.	Liquid Coating Composition								
	Resin Component								Solvent
	1st component		2nd component		3rd component		Inherent viscosity (η inh)	Resin concentration (% by wt.)	
	Kind	mol %	Kind	mol %	Kind	mol %			
Ex. 16	VF	70	HFP	30	—	—	0.71	30	Acetic acid
Comp. Ex. 22	VDF	70	HFP	30	—	—	0.67	30	Acetic acid
Ex. 17	VF	92	HFP	8	—	—	0.74	10	Acetic acid
Comp. Ex. 23	VDF	92	HFP	8	—	—	0.70	10	Acetic acid
Comp. Ex. 24	VF	97	HFP	3	—	—	0.80	10	Acetic acid
Ex. 18	VF	55	HFP	45	—	—	0.58	30	Acetic acid
Comp. Ex. 25	VDF	55	HFP	45	—	—	0.54	30	Acetic acid
Comp. Ex. 26	VF	45	HFP	55	—	—	0.55	30	Acetic acid
Ex. 19	VF	75	HFP	25	—	—	0.66	30	Propionic acid
Comp. Ex. 27	VDF	75	HFP	25	—	—	0.61	30	Propionic acid
Comp. Ex. 28	VF	98.2	HFP	2.8	—	—	0.77	10	Propionic acid
Comp. Ex. 29	VF	43	HFP	57	—	—	0.53	30	Propionic acid
Ex. 20	VF	60	HFP	40	—	—	0.59	30	Acetic anhydride
Comp. Ex. 30	VDF	60	HFP	40	—	—	0.53	30	Acetic anhydride

TABLE 2 (continued).

No.	Liquid Coating Composition								
	Resin Component								
	1st component		2nd component		3rd component		Inherent viscosity (η inh)	Resin concentration (% by wt.)	Solvent
	Kind	mol %	Kind	mol %	Kind	mol %			
Comp. Ex. 31	VF	60	HFP	40	—	—	0.59	10	Formic acid
Ex. 21	VF	73.2	HFP	24.0	VAc	2.8	0.67	30	Acetic acid
Comp. Ex. 32	VDF	73.2	HFP	24.0	VAc	2.8	0.65	30	Acetic acid
Ex. 22	VF	65	HFP	35	—	—	0.59	30	Diethyl oxalate
Comp. Ex. 33	VDF	65	HFP	35	—	—	0.55	30	Diethyl oxalate
Ex. 23	VF	90	HFP	10	—	—	0.75	10	Diethyl oxalate
Comp. Ex. 34	VDF	90	HFP	10	—	—	0.73	10	Diethyl oxalate
Comp. Ex. 35	VF	98	HFP	2	—	—	0.79	10	Diethyl oxalate
Ex. 24	VF	56	HFP	44	—	—	0.51	30	Diethyl oxalate
Comp. Ex. 36	VDF	56	HFP	44	—	—	0.51	30	Diethyl oxalate
Comp. Ex. 37	VF	44	HFP	56	—	—	0.50	30	Diethyl oxalate
Ex. 25	VF	80	HFP	20	—	—	0.73	20	Diethyl malonate
Comp. Ex. 38	VDF	80	HFP	20	—	—	0.63	20	Diethyl malonate
Comp. Ex. 39	VF	97	HFP	3	—	—	0.78	10	Diethyl malonate
Comp. Ex. 40	VF	46	HFP	54	—	—	0.60	30	Diethyl malonate
Ex. 26	VF	74.7	HFP	25.0	AA	0.3	0.63	30	Diethyl malonate
Comp. Ex. 41	VDF	74.7	HFP	25.0	AA	0.3	0.66	30	Diethyl malonate

TABLE 2 (continued).

No.	Liquid Coating Composition								
	Resin Component								
	1st component		2nd component		3rd component		Inherent viscosity (η inh)	Resin concentration (% by wt.)	Solvent
	Kind	mol %	Kind	mol %	Kind	mol %			
Ex. 27	VF	58	HFP	42	—	—	0.55	30	Dimethyl adipate
Comp. Ex. 42	VDF	58	HFP	42	—	—	0.51	30	Dimethyl adipate
Ex. 28	VF	65	HFP	35	—	—	0.59	30	Tetrahydrofuran
Comp. Ex. 43	VDF	65	HFP	35	—	—	0.55	30	Tetrahydrofuran
Ex. 29	VF	90.5	HFP	9.5	—	—	0.81	10	Tetrahydrofuran
Comp. Ex. 44	VDF	90.5	HFP	9.5	—	—	0.74	10	Tetrahydrofuran
Comp. Ex. 45	VF	97	HFP	3	—	—	0.78	10	Tetrahydrofuran
Ex. 30	VF	55	HFP	45	—	—	0.63	30	Tetrahydrofuran
Comp. Ex. 46	VDF	55	HFP	45	—	—	0.53	30	Tetrahydrofuran
Comp. Ex. 47	VF	45	HFP	55	—	—	0.54	30	Tetrahydrofuran
Ex. 31	VF	58	HFP	42	—	—	0.55	30	1,3-Dioxane
Comp. Ex. 48	VDF	58	HFP	42	—	—	0.51	30	1,3-Dioxane
Ex. 32	VF	74.7	HFP	25.0	GMA	0.3	0.70	30	1,3-Dioxane
Comp. Ex. 49	VDF	74.7	HFP	25.0	GMA	0.3	0.67	30	1,3-Dioxane
Comp. Ex. 50	VF	73.4	HFP	25.0	GMA	1.6	0.66	10	1,3-Dioxane
Ex. 33	VF	73	HFP	27	—	—	0.61	30	1,3-Dioxane
Comp. Ex. 51	VF	73	HFP	27	—	—	0.61	10	Ethyleneglycol monomethylether

TABLE 2 (continued).

No.	Liquid Coating Composition								
	Resin Component								
	1st component		2nd component		3rd component		Inherent viscosity (η inh)	Resin concentration (% by wt.)	Solvent
	Kind	mol %	Kind	mol %	Kind	mol %			
Comp. Ex. 52	VF	73	HFP	27	—	—	0.61	10	Ethylether
Ex. 34	VF	73	HFP	27	—	—	0.61	30	Acetonitrile
Comp. Ex. 53	VDF	73	HFP	27	—	—	0.58	30	Acetonitrile
Ex. 35	VF	89	HFP	11	—	—	0.81	10	Acetonitrile
Comp. Ex. 54	VDF	89	HFP	11	—	—	0.75	10	Acetonitrile
Comp. Ex. 55	VF	97	HFP	3	—	—	0.78	10	Acetonitrile
Ex. 36	VF	58	HFP	42	—	—	0.55	30	Acetonitrile
Comp. Ex. 55	VDF	58	HFP	42	—	—	0.51	30	Acetonitrile
Comp. Ex. 56	VF	42	HFP	58	—	—	0.60	30	Acetonitrile
Ex. 37	VF	74.7	HFP	25.0	GMA	0.3	0.70	30	Acetonitrile
Comp. Ex. 57	VDF	74.7	HFP	25.0	GMA	0.3	0.67	30	Acetonitrile
Ex. 38	VF	73	HFP	27	—	—	0.61	30	Propionitrile
Comp. Ex. 58	VDF	73	HFP	27	—	—	0.58	30	Propionitrile
Ex. 39	VF	88	HFP	12	—	—	0.79	10	Propionitrile
Comp. Ex. 59	VDF	88	HFP	12	—	—	0.77	10	Propionitrile
Comp. Ex. 60	VF	97	HFP	3	—	—	0.78	10	Propionitrile
Ex. 40	VF	57	HFP	43	—	—	0.57	30	Propionitrile
Comp. Ex. 61	VDF	57	HFP	43	—	—	0.57	30	Propionitrile

TABLE 2 (continued).

No.	Liquid Coating Composition								
	Resin Component								Solvent
	1st component		2nd component		3rd component		Inherent viscosity (η inh)	Resin concentration (% by wt.)	
	Kind	mol %	Kind	mol %	Kind	mol %			
Comp. Ex. 62	VF	43	HFP	57	—	—	0.60	30	Propionitrile
Ex. 41	VF	73	HFP	27	—	—	0.61	30	Adiponitrile
Comp. Ex. 63	VDF	73	HFP	27	—	—	0.58	30	Adiponitrile

TABLE 2 (continued).

No.	Properties				
	Storage stability (hr)	Tensile strength (Kg/cm²)	Elongation (%)	Initial Young's modulus (kg/cm²)	Transparency (%)
Ex. 16	360	218	281	2,530	87
Comp. Ex. 22	5	106	441	13	60
Ex. 17	240	342	291	4,600	90
Comp. Ex. 23	6	168	513	83	57
Comp. Ex. 24	(Partially insoluble)				
Ex. 18	over 720	179	493	230	83
Comp. Ex. 25	10	84	730	12	62
Comp. Ex. 26	over 720	99	611	47	82
Ex. 19	480	238	277	1,980	90
Comp. Ex. 27	7	98	433	15	55
Comp. Ex. 28	(Insoluble)				
Comp. Ex. 29	over 720	95	513	45	87
Ex. 20	over 720	178	413	731	90
Comp. Ex. 30	7	78	555	11	53
Comp. Ex. 31	(Insoluble)				
Ex. 21	240	221	310	3,230	88
Comp. Ex. 32	3	101	481	60	57
Ex. 22	over 720	199	318	1,080	91
Comp. Ex. 33	6	81	513	12	59
Ex. 23	240	339	218	4,730	91
Comp. Ex. 34	7	173	613	83	60
Comp. Ex. 35	(Insoluble)				
Ex. 24	over 720	181	731	538	87

TABLE 2 (continued).

No.	Properties				
	Storage stability (hr)	Tensile strength (Kg/cm^2)	Elongation (%)	Initial Young's modulus (kg/cm^2)	Transparency (%)
Comp. Ex. 36	7	83	740	12	60
Comp. Ex. 37	over 720	77	430	49	89
Ex. 25	480	294	215	4,500	90
Comp. Ex. 38	6	112	531	30	59
Comp. Ex. 39		(Partially insoluble)			
Comp. Ex. 40	over 720	85	483	60	85
Ex. 26	120	231	433	3,940	87
Comp. Ex. 41	3	112	495	60	55
Ex. 27	240	182	269	113	83
Comp. Ex. 42	5	78	483	11	57
Ex. 28	over 720	199	318	1,080	88
Comp. Ex. 43	10	81	513	12	58
Ex. 29	240	340	269	4,300	90
Comp. Ex. 44	10	180	317	70	61
Comp. Ex. 45		(Partially insoluble)			
Ex. 30	over 720	180	531	630	90
Comp. Ex. 46	10	84	738	12	62
Comp. Ex. 47	over 720	99	611	47	80
Ex. 31	over 720	182	269	113	87
Comp. Ex. 48	7	78	483	11	60
Ex. 32	over 720	228	315	3,120	88
Comp. Ex. 49	4	106	428	61	58
Comp. Ex. 50		(Partially insoluble)			
Ex. 33	over 720	231	267	2,170	87
Comp. Ex. 51		(Insoluble)			
Comp. Ex. 52		(Insoluble)			

TABLE 2 (continued).

No.	Properties					
	Storage stability (hr)	Tensile strength (Kg/cm^2)	Elongation (%)	Initial Young's modulus (kg/cm^2)	Transparency (%)
Ex. 34	over 720	231	267	2,170	87
Comp. Ex. 53	6	95	613	14	60
Ex. 35	240	339	271	4,650	83
Comp. Ex. 54	10	169	477	83	58
Comp. Ex. 55		(Partially insoluble)			
Ex. 36	360	182	269	113	84
Comp. Ex. 55	7	78	483	11	60
Comp. Ex. 56	over 720	80	432	52	86
Ex. 37	over 720	228	315	3,120	89
Comp. Ex. 57	5	106	428	61	57
Ex. 38	over 720	231	267	2,160	89
Comp. Ex. 58	10	95	613	14	60
Ex. 39	168	340	269	4,570	88
Comp. Ex. 59	10	169	477	83	56
Comp. Ex. 60		(Insoluble)			
Ex. 40	over 720	177	534	620	90
Comp. Ex. 61	10	80	740	12	58
Comp. Ex. 62	over 720	82	433	115	79
Ex. 41	240	231	267	2,170	81
Comp. Ex. 63	3	95	613	14	60

Examples 42 to 50 and
Comparative Examples 64 to 72.

Using solvents of group (7) mentioned hereinabove, liquid coating compositions were prepared in the same way as set forth in Example 6. The results are given in Table 3.

TABLE 3.

No.	Liquid Coating Composition								
	Resin Component						Inherent viscosity (η inh)	Resin concentration (% by wt.)	Solvent
	1st component		2nd component		3rd component				
	Kind	mol %	Kind	mol %	Kind	mol %			
Ex. 42	VF	65	HFP	35	—	—	0.59	30	Diethyl carbonate
Comp. Ex. 64	VDF	65	HFP	35	—	—	0.55	30	Diethyl carbonate
Ex. 43	VF	52	HFP	48	—	—	0.50	30	Ethylene carbonate
Comp. Ex. 65	VDF	52	HFP	48	—	—	0.51	30	Ethylene carbonate
Ex. 44	VF	80	HFP	20	—	—	0.73	20	Cyclohexanone
Comp. Ex. 66	VDF	80	HFP	20	—	—	0.63	20	Cyclohexanone
Ex. 45	VF	60	HFP	40	—	—	0.59	30	N,N-dimethyl formamide
Comp. Ex. 67	VDF	60	HFP	40	—	—	0.53	30	N,N-dimethyl formamide
Ex. 46	VF	80	HFP	20	—	—	0.73	20	N,N-dimethyl acetamide
Comp. Ex. 68	VDF	80	HFP	20	—	—	0.63	20	N,N-dimethyl acetamide
Ex. 47	VF	73	HFP	27	—	—	0.61	30	Dimethyl sulfoxide
Comp. Ex. 69	VDF	73	HFP	27	—	—	0.58	30	Dimethyl sulfoxide
Ex. 48	VF	58	HFP	42	—	—	0.55	30	N-Methyl pyrrolidone
Comp. Ex. 70	VDF	58	HFP	42	—	—	0.51	30	N-Methyl pyrrolidone
Ex. 49	VF	75	HFP	25	—	—	0.66	30	γ-Butyrolactone
Comp. Ex. 71	VDF	75	HFP	25	—	—	0.61	30	γ-Butyrolactone
Ex. 50	VF	74.6	HFP	25.0	GMA	0.4	0.53	30	N,N-dimethyl formamide
Comp. Ex. 72	VDF	74.6	HFP	25.0	GMA	0.4	0.55	30	N,N-dimethyl formamide

TABLE 3 (continued).

No.	Properties				
	Storage stability (hr)	Tensile strength (Kg/cm^2)	Elongation (%)	Initial Young's modulus (kg/cm^2)	Transparency (%)
Ex. 42	over 720	199	318	1,080	88
Comp. Ex. 64	10	81	513	12	56
Ex. 43	over 720	171	531	135	84
Comp. Ex. 65	10	67	667	10	59
Ex. 44	360	294	215	4,500	90
Comp. Ex. 66	10	112	530	31	59
Ex. 45	over 720	178	413	731	89
Comp. Ex. 67	3	78	555	11	53
Ex. 46	240	294	215	4,500	90
Comp. Ex. 68	6	112	531	30	60
Ex. 47	over 720	231	267	2,170	76
Comp. Ex. 69	7	95	613	14	54
Ex. 48	over 720	182	269	113	87
Comp. Ex. 70	6	78	483	11	55
Ex. 49	480	238	277	2,000	89
Comp. Ex. 71	10	98	433	15	55
Ex. 50	over 720	238	306	4,120	88
Comp. Ex. 72	6	101	418	60	55

Examples 51 to 55 and Comparative Examples 73 to 79.

Liquid coating compositions were prepared using a copolymer having an inherent viscosity of 0.71 and derived from 70.7 mol % of vinyl fluoride and 29.3 mol % of hexafluoropropylene and various solvents. The results are given in Table 4.

TABLE 4.

No.	Solvent A	Solvent B	Solvent C	A/B/C (wt. %)	Resin concentration (% by wt.)	Properties: Storage stability (hr.)	Tensile strength (kg/cm²)	Elongation (%)	Initial young's modulus (kg/cm²)	Transparency (%)
Ex. 51	Acetone	Butyl acetate		1/1	30	over 720	220	273	2,340	88
Ex. 52	Methylethyl ketone	Methylisobutyl ketone		3/2	30	over 720	220	273	2,340	89
Ex. 53	Methylethyl ketone	Methylisobutyl ketone		1/1	30	over 720	220	273	2,340	90
Ex. 54	Methylethyl ketone	Methylisobutyl ketone	Cellosolve acetate	1/2/1	30	over 720	220	273	2,340	92
Ex. 55	Butyl acetate	Isoamylacetate	Cellosolve acetate	1/2/1	30	over 720	220	273	2,340	90
Comp. Ex. 73	Methylethyl ketone	Formic acid		3/2	30	(Partially insoluble)				
Comp. Ex. 74	Methylethyl ketone	Methyl laurate		3/2	30	(Partially insoluble)				
Comp. Ex. 75	Methylethyl ketone	Ethyleneglycol monomethylether		3/2	30	(Partially insoluble)				
Comp. Ex. 76	Methylethyl ketone	Methylphenyl ketone		3/2	30	(Partially insoluble)				
Comp. Ex. 77	Methylethyl ketone	Benzylacetate		3/2	30	(Partially insoluble)				
Comp. Ex. 78	Methylethyl ketone	Methyl salicylate		3/2	30	(Partially insoluble)				
Comp. Ex. 79	Methylethyl ketone	Methyl benzoate	Cellosolve acetate	1/2/1	30	(Partially insoluble)				

(Cellosolve is a registered Trade Mark)

Examples 56 to 62 and
Comparative Examples 80 to 87.

A polished steel plate (90x70x1 mm) which had been thoroughly degreased and cleansed, polished with water proof polishing paper No. 280, washed with water, immersed in ethyl alcohol and air dried was coated with Epilite 400 Red Red primer in a film thickness of 20 microns. After drying in the air, a secondary primer of the following formulation was coated thereon.

Formulation of the secondary primer

Copolymer (η_{inh}=0.28) composed of (A), (B), (C) and (D):	35 parts by weight
(A) Methyl methacrylate	66.5 % by weight
(B) Butyl acrylate	19.0 % by weight
(C) 2-Ethylhexyl acrylate	9.5 % by weight
(D) Acrylic acid	5.0 % by weight
Methyl ethyl ketone	30 parts by weight
Toluene	35 parts by weight
Zinc chromatic C	10 parts by weight

After coating, the coated layer (thickness 10 microns) was dried in air for 20 hours. On top of the secondary coating, a liquid composition having a thickness of 20 microns and consisting of the resin components, solvents, and additives shown in Table 5 was coated. The coated layer was dried in the air for 48 hours. The properties of the coating layer after air drying are shown in Table 5.

TABLE 5.

No.	Liquid Coating Composition							
	Resin Component							
	1st component		2nd component		3rd component		Inherent viscosity (η inh)	Resin concentration (% by wt.)
	Kind	mol %	Kind	mol %	Kind	mol %		
Ex. 56	VF	70	HFP	30	—	—	0.31	30
Comp. Ex. 80	VDF	70	HFP	30	—	—	0.32	30
Ex. 57	VF	70	HFP	30	—	—	0.31	30
Comp. Ex. 81	VDF	70	HFP	30	—	—	0.32	30
Ex. 58	VF	75	HFP	25	—	—	0.26	30
Comp. Ex. 82	VDF	75	HFP	25	—	—	0.25	30
Ex. 59	VF	74.7	HFP	25	GMA	0.3	0.52	30
Comp. Ex. 83	VDF	74.7	HFP	25	GMA	0.3	0.51	30
Ex. 60	VF	55	HFP	45	—	—	0.40	30
Comp. Ex. 84	VDF	55	HFP	45	—	—	0.38	30
Comp. Ex. 85	VF	45	HFP	55	—	—	0.41	30
Ex. 61	VF	74.5	HFP	25	GMA	0.5	0.30	30
Comp. Ex. 86	VDF	74.5	HFP	25	GMA	0.5	0.29	30
Ex. 62	VF	70	HFP	30	—	—	0.41	30
Comp. Ex. 87	VDF	70	HFP	30	—	—	0.39	30

TABLE 5 (Continued).

No.	Liquid Coating Composition: Solvent A (weight ratio)	Solvent B (weight ratio)	Solvent C (weight ratio)	Additives A (wt. %)	Additives B (wt. %)	Additives C (wt. %)	Properties: Storage stability (hr)	Pencil hardness	Gloss
Ex. 56	Methyl ethyl ketone 1	Butyl acetate 1		TiO_2 9	—	—	over 720	HB	40
Comp. Ex. 80	Methyl ethyl ketone 1	Butyl acetate 1		TiO_2 9	—	—	6	2B—B	15
Ex. 57	Butyl acetate 1	Isoamyl acetate 2	Cellosolve acetate 1	TiO_2 9	—	—	over 720	HB	60
Comp. Ex. 81	Butyl acetate 1	Isoamyl acetate 2	Cellosolve acetate 1	TiO_2 9	—	—	7	2B—B	20
Ex. 58	Butyl acetate 1	Isoamyl acetate 2	Cellosolve acetate 1	TiO_2 9	Talc 1	—	over 720	HB—H	55
Comp. Ex. 82	Butyl acetate 1	Isoamyl acetate 2	Cellosolve acetate 1	TiO_2 9	Talc 1	—	9	B	17
Ex. 59	Butyl acetate 1	Isoamyl acetate 2	Cellosolve acetate 1	TiO_2 9	—	—	over 720	H	35
Comp. Ex. 83	Butyl acetate 1	Isoamyl acetate 2	Cellosolve acetate 1	TiO_2 9	—	—	5	B	13
Ex. 60	Methyl ethyl ketone 1	Butyl acetate 1		TiO_2 9	Talc 5	—	over 720	B—HB	62
Comp. Ex. 84	Methyl ethyl ketone 1	Butyl acetate 1		TiO_2 9	Talc 5	—	10	2B	22
Comp. Ex. 85	Methyl ethyl ketone 1	Butyl acetate 1		TiO_2 9	Talc 5	—	over 720	2B	65

TABLE 5 (Continued).

No.	Liquid Coating Composition: Solvent A (weight ratio)	Solvent B (weight ratio)	Solvent C (weight ratio)	Additives A (wt. %)	Additives B (wt. %)	Additives C (wt. %)	Properties: Storage stability (hr)	Pencil hardness	Gloss
Ex. 61	Methyl ethyl ketone 1	Butyl acetate 2	Isoamyl acetate 1	TiO_2 9	—	—	over 720	HB—H	45
Comp. Ex. 86	Methyl ethyl ketone 1	Butyl acetate 2	Isoamyl acetate 1	TiO_2 9	—	—	10	B	18
Ex. 62	Methyl ethyl ketone 1	Butyl acetate 2	Isoamyl acetate 1	TiO_2 9	Dimethyl phthalate 0.2	Poly(methyl methacrylate) 1	over 720	HB	57
Comp. Ex. 87	Methyl ethyl ketone 1	Butyl acetate 2	Isoamyl acetate 1	TiO_2 9	Dimethyl phthalate 0.2	Poly(methyl methacrylate 1	8	2B	23

Examples 63 to 67 and
Comparative Examples 88 to 92.

The copolymer, the cross-linking agent and additive were dissolved in methyl ethyl ketone so that the solids content of the copolymer became 20 % by weight. A coated layer was prepared from the composition obtained. The coated layer was cured at different temperatures for various periods of time. The results are shown in Table 6.

TABLE 6.

No.	Resin Component							Cross-linking agent	
	1st component		2nd component		3rd component		Inherent viscosity	Kind	Amount based on the resin
	Kind	mol %	Kind	mol %	Kind	mol %			
Ex. 63	VF	90	HFP	10	—	—	0.81	Triethylene tetramine	5 wt.%
Comp. Ex. 88	VDF	90	HFP	10	—	—	0.79	Triethylene tetramine	5 wt.%
Ex. 64	VF	84	HFP	16	—	—	0.77	Hexamethylene diamine	5 wt.%
Comp. Ex. 89	VDF	84	HFP	16	—	—	0.78	Hexamethylene diamine	5 wt.%
Ex. 65	VF	80	HFP	20	—	—	0.80	Triethylene tetramine	5 wt.%
Comp. Ex. 90	VDF	80	HFP	20	—	—	0.81	Triethylene tetramine	5 wt.%
Ex. 66	VF	70	HFP	30	—	—	0.67	Triethylene tetramine	5 wt.%
Comp. Ex. 91	VDF	70	HFP	30	—	—	0.52	Triethylene tetramine	5 wt.%
Ex. 67	VF	74.7	HFP	25	GMA	0.3	0.52	Triethylene tetramine	5 wt.%
Comp. Ex. 92	VDF	74.7	HFP	25	GMA	0.3	0.49	Triethylene tetramine	5 wt.%

TABLE 6(continued).

No.	Additives				Baking Conditions		Properties of Coated Film		
	A		B						
	Kind	Amount based on the resin	Kind	Amount based on the resin	Temp. (0°C)	Time (Min.)	Tensile strength (kg./cm²)	Elongation (%)	Initial Young's modulus (kg/cm²)
Ex. 63	—	—	—	—	200	15	362	48	23,400
Comp. Ex. 88	—	—	—	—	200	15	201	185	162
Ex. 64	—	—	—	—	180	20	294	50	25,120
Comp. Ex. 89	—	—	—	—	180	20	188	195	100
Ex. 65	Carbon black	20 wt.%	—	—	230	5	287	47	27,300
Comp. Ex. 90	Carbon black	20 wt.%	—	—	230	5	167	201	97
Ex. 66	Carbon black	20 wt.%	MgO	10 wt.%	200	10	267	43	26,700
Comp. Ex. 91	Carbon black	20 wt.%	MgO	10 wt.%	200	10	166	198	100
Ex. 67	Carbon black	20 wt.%	MgO	10 wt.%	200	10	348	55	29,800
Comp. Ex. 92	Carbon black	20 wt.%	MgO	10 wt.%	200	10	180	189	98

WHAT WE CLAIM IS:—

1. A liquid coating composition comprising a vinyl fluoride/hexafluoropropylene copolymer having an inherent viscosity (measured as hereinbefore defined) of 0.1 to 2 and composed of (i) 5 to 50 mol % of units derived from hexafluoropropylene, (ii) 0 to 10 mol % of units derived from a vinyl ester of an aliphatic carboxylic acid, in which the acid portion has 1 to 6 carbon atoms, or 0 to 1 mol % of units derived from a monomer which is selected from unsaturated aliphatic carboxylic acids having 3 to 6 carbon atoms, glycidyl acrylate and glycidyl methacrylate and (iii) the remainder being units derived from vinyl fluoride, and a solvent for the copolymer which is one or more of (1) an aliphatic ketone having not more than 9 carbon atoms, (2) an alkyl ester of an aliphatic monocarboxylic acid or a halide thereof, the said ester having not more than 10 carbon atoms, (3) an alkyl ester of an aliphatic dicarboxylic acid, the acid residue having 2 to 7 carbon atoms and each alkyl group having not more than 3 carbon atoms, (4) an aliphatic monocarboxylic acid having 2 to 4 carbon atoms or an anhydride thereof, (5) a cyclic ether, (6) an aliphatic nitrile having 2 to 6 carbon atoms, and (7) a compound selected from dialkyl esters of carbonic acid, wherein the alkyl groups together contain 2 to 4 carbon atoms, ethylene carbonate, cyclohexanone, N,N-dimethyl formamide, N,N-dimethyl acetamide, dimethyl sulfoxide, N-methyl pyrrolidone and γ-butyrolactone, the amount of the said copolymer being 1 to 50% by weight, as solids content, based on the weight of the composition.

2. A composition according to claim 1, wherein the said copolymer comprises 10 to 50 mol % of units derived from hexafluoropropylene, with the remainder being units derived from vinyl fluoride.

3. A composition according to claim 1 or 2 in which the copolymer has an inherent viscosity of 0.1 to 1.

4. A composition according to any one of the preceding claims which further contains an additive selected from coloring agents, viscosity control agents, wetting agents, plasticizers, light stabilizers, antioxidants, defoamers, cross-linking promotors.

5. A composition according to Claim 4 which contains a cross-linking agent selected from aliphatic polyamines, aromatic polyamines and carbamate derivatives thereof, and a cross-linking promotor selected from oxides of alkaline earth metals.

6. A composition according to any one of the preceding claims, which further contains another resin soluble in said solvent, in an amount up to 5% by weight based on the weight of the composition.

7. A composition according to any one of the preceding claims wherein the said copolymer is one which has been prepared by aqueous suspension polymerization of (i) 5 to 50 mol % of hexafluoropropylene, (ii) 0 to 10 mol % of a vinyl ester of an aliphatic carboxylic acid in which the acid portion has 1 to 6 carbon atoms, or 0 to 1 mol % of a monomer selected from unsaturated aliphatic carboxylic acids having 3 to 6 carbon atoms, glycidyl acrylate and glycidyl methacrylate, and (iii) vinyl fluoride, in the presence of an organic peroxide initiator, a fluorine-containing surface active agent and a dispersing agent.

8. A composition according to Claim 7 wherein the said copolymer has been prepared in the presence of a molecular-weight regulating agent selected from trichlorofluoromethane, 1,2-difluoro-1,1,2,2-tetrachloroethane and 1,1,2-trifluoro-1,2,2-trichloroethane.

9. A composition according to Claim 1 substantially as hereinbefore described.

10. A composition according to Claim 1 substantially as described in any one of the foregoing Examples.

11. A process for preparing a coating on a substrate which comprises applying to the substrate a coating composition as claimed in any one of the preceding claims.

12. A process according to Claim 11 wherein the copolymer is cross-linked by heating after the composition has been applied to the substrate.

13. A coated substrate prepared by a process as claimed in claim 11 or 12.

14. A composition according to claim 2 in which the copolymer has an inherent viscosity of 0.1 to 1.0.

15. A composition according to claim 14 in which the solvent is selected from those solvents listed under items (1) to (6) of claim 1, N,N-dimethyl formamide, N,N-dimethyl acetamide, dimethyl sulfoxide, N-methyl pyrrolidone and γ-butyrolactone.

J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square, Gray's Inn,
London WC1R 5EU.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.